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Current Uses and Future Prospects

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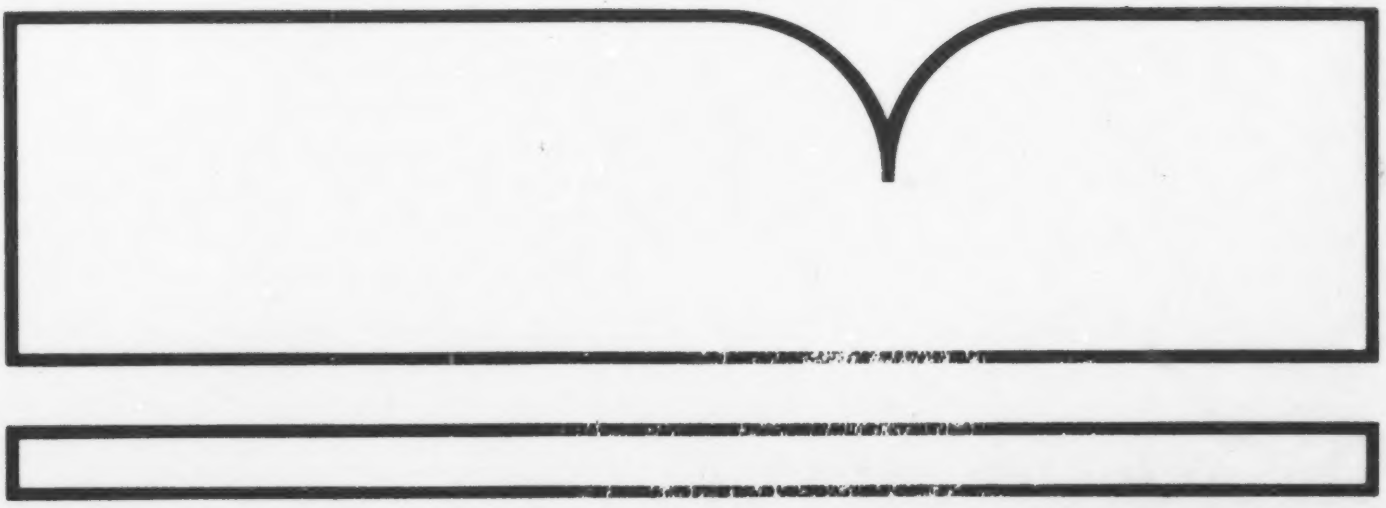

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16. ABSTRACT

Currently, the most popular method of analyzing total organic halide in water involves carbon adsorption, oxidative combustion, and measurement of the hydrogen halide by microcoulometry. Total organic halide can be used as an indicator of water quality, providing a direct measure of disinfection by-product formation, and in some circumstances, a surrogate measure of individual organic pollutants. An important application of organic halide measurements is in unit process design, control, and monitoring. Each potential application, however, must be carefully assessed to determine the usefulness of organic halide measurements.

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Organic Halogen Measurements: Current Uses and Future Prospects

Alan A. Stevens, Ronald C. Dressman, R. Kent Sorrell, and Herbert J. Brass

Currently, the most popular method of analyzing total organic halide in water involves carbon adsorption, oxidative combustion, and measurement of the hydrogen halide by microcoulometry. Total organic halide can be used as an indicator of water quality, providing a direct measure of disinfection by-product formation and, in some circumstances, a surrogate measure of individual organic pollutants. An important application of organic halide measurements is in unit process design, control, and monitoring. Each potential application, however, must be carefully assessed to determine the usefulness of organic halide measurements.

In the early 1970s, in an effort to measure the removal of halogenated organic compounds by granular activated carbon (GAC) filters at water treatment plants along the Rhine River, Kühn and Sontheimer[1,2] developed a technique that measured the total organic chlorine (TOCl) adsorbed on the GAC at various depths of the filter, thus defining the adsorption wave front. The halogenated compounds found in the Rhine[3] were not naturally occurring and were, therefore, considered undesirable in a finished drinking water. The location of the adsorption wave front gave important information about the carbon filters' ability to continue to remove these pollutants. Exhaustion of the GAC signaled the need for reactivation.

Kühn developed a pyrohydrolysis procedure that involved the combustion of a 1-g GAC sample in an atmosphere of oxygen and steam, followed by analysis of the liberated chloride with an ion-specific electrode. Superheated steam and oxygen were passed through two furnaces in series that had a common

combustion tube. The first furnace was heated from ambient temperature to 700°C, and the second was maintained at 1000°C. The hydrogen chloride (HCl) produced during pyrohydrolysis was collected as the pyrohydrolyzate by condensing the steam. Further investigation, by Kühn et al[4] led to techniques for measuring the TOCl content of the water itself.

Carbon adsorption techniques

The first step in Kühn and Sontheimer's procedure involved the adsorption of organic compounds in the water onto ground GAC. This was accomplished by adding 1 g of the GAC to a 10-L water sample and stirring for 1 h. This batch extraction was repeated a second time after recovering the GAC by a process of flocculation, sedimentation, siphoning off the water, and membrane filtration.

The recovered carbon, in the form of a sludge from each extraction, was then pyrohydrolyzed to convert organochlorine compounds to HCl. The chloride (Cl^-) in the pyrohydrolyzate was measured with an ion-specific electrode. To account for interference from inorganic Cl^- adsorbed onto the activated carbon, a duplicate sample was extracted in the same way, and the recovered activated carbon sludge was washed in a solution of sodium nitrate for a minimum of 6 h. During this process, nitrate (NO_3^-) displaced inorganic Cl^- from the carbon, and the Cl^- in the wash water was then measured with the ion-specific probe. The Cl^- contributed by organochlorine compounds was calculated by subtracting the amount of Cl^- measured in the nitrate-washed sample from the amount of Cl^- measured in the pyrohydrolyzate. This value was termed TOCl because it was obtained with a chloride-ion-specific electrode.

As a result of an evaluation[5] by the Drinking Water Research Division (DWRD) of the Municipal Environmental Research Laboratory, US Environmental Protection Agency (USEPA), Cincinnati, Ohio, the method of Kühn and Sontheimer was modified. Microcoulometry was selected to measure the Cl^- because a positive bias associated with the use of the ion-specific electrode had been recognized to produce values up to 10 times the true value in some surface water samples. The selection of the microcoulometric detector also increased sensitivity 100-fold, reducing the necessary sample size to 100 mL or less. The measurement was redefined as carbon adsorbable organohalides reported as Cl^- (CAOX as Cl^-), recognizing that only the carbon-adsorbable fraction of TOCl (90–95 percent as inferred from measured total organic carbon [TOC] adsorption) was being accounted for and that bromide (Br^-) and iodide (I^-), when present, were also being titrated. Next, inorganic halide (X^-) was excluded from the adsorption process by the addition of NO_3^- to the sample, thus eliminating the need for a duplicate sample to correct for inorganic Cl^- interference and also avoiding the 6-h delay in obtaining results. Finally, the X^- contributed by organohalides was determined directly on the activated carbon sludge with samples that had been pretreated to exclude the adsorption of inorganic X^- onto the carbon; this allowed increased reproducibility and much greater accuracy.

Evaluation of the Kühn batch method led to the development of a minicolumn method[6] for adsorbing organohalides onto activated carbon. The instrumentation* for this method was developed under contract to USEPA. Subsequent evaluation of the minicolumn method by DWRD[7] led to modifications being made by the instrument manufacturer so that as little as 5 μg organic halide (OX)/L of water could be measured by oxidative combustion of the carbon. This measurement is generally referred to as total organic halide (TOX) and is the basis of USEPA Method 450.1, Total Organic Halogen.†

In addition to the instrumentation that was developed under contract to USEPA, a second instrument system‡ is now being marketed in the United States that consists of a TOX analytical module and an adsorpton module based on USEPA Method 450.1.

A small batch (100 mL) extraction method using activated carbon,[8] which is a hybrid of the modified Kühn method[5] and the minicolumn method for water samples,[6] has also been developed. Activated carbon recovery is by membrane filtration, without the need for flocculation and sedimentation. Pyrolysis and

*DX-20, Xertex Dohrmann, Santa Clara, Calif.
†Environmental Monitoring and Support Laboratory, Cincinnati, Ohio
‡TOX-10, Mitsubishi Chemical Industries Ltd., through Cosa Instrument Corp., Norwood, N.J.

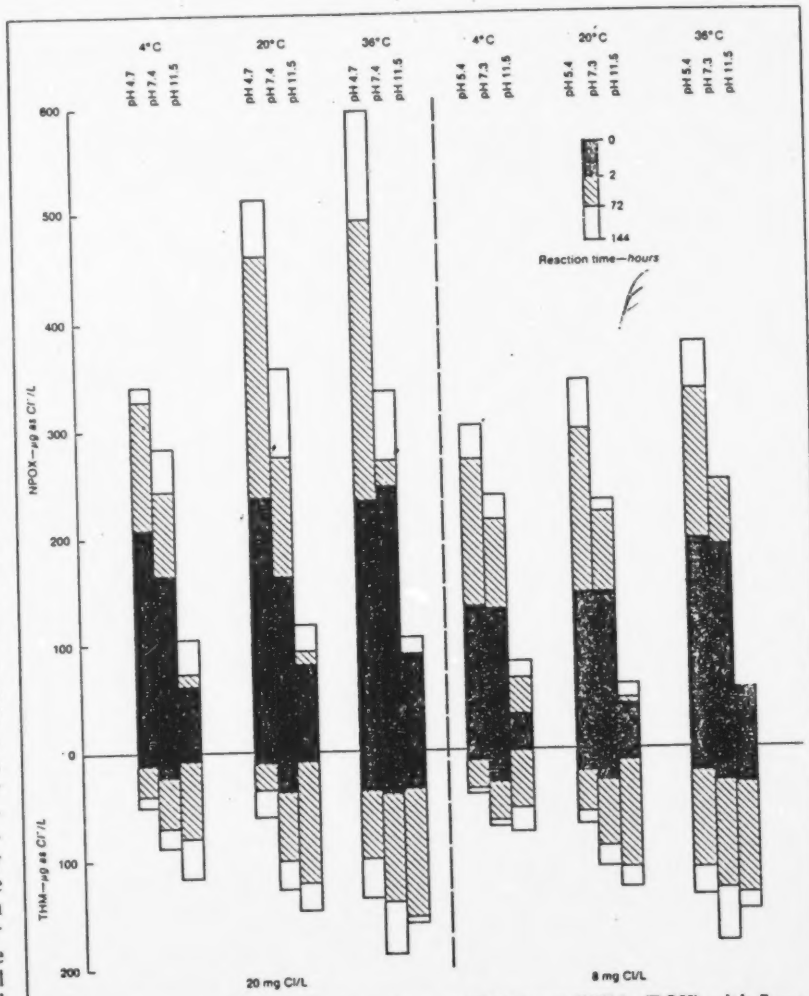

Figure 1. A comparison of the formation of NPOX and THMs (POX) with 5 mg humic acid/L at three temperatures, three pH values, and two chlorine dosages *(NPOX + POX = TOX)*

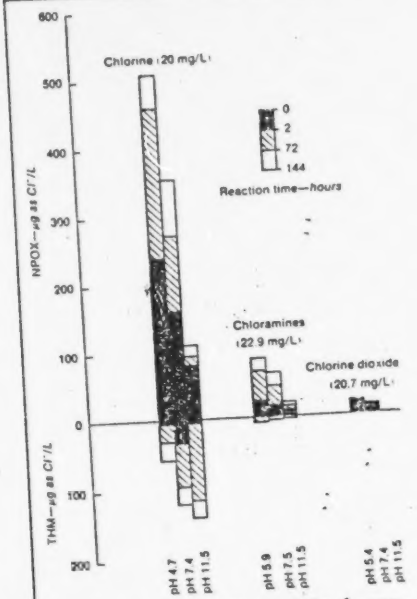

Figure 2. A comparison of the formation of NPOX and THMs (POX) in distilled water solutions of 5 mg humic acid/L at 20°C and with various disinfectants *(NPOX + POX = TOX)*

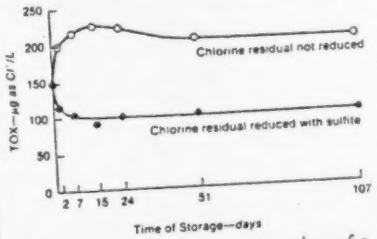

Figure 3. The TOX concentration of a chlorinated surface water stored at 20°C

TABLE 1

Reported accuracy of TOX analysis for volatile organohalides in reagent water

Model Compounds	Concentration μg/L	Average Recovery *percent*	Reference
Chloroform	98	89	7
	112	94	24
Bromodichloromethane	160	98	7
Dibromochloromethane	155	86	7
	374	73	7
Bromoform	160	110	7
	238	100	24
Bromobenzene	443	95	24

TABLE 2

Recovery of various compounds spiked into reagent water (1000 μg/L) by direct POX determination[26]

Compound	Recovery* *percent*
Methylene chloride	87 (4)
Chloroform	81 (3)
trans-1,2-Dichloroethylene	106 (0.2)
1,1-Dichloroethane	84 (3)
1,1-Dichloroethylene	78 (2)
1,1,2,2-Tetrachloroethane	88 (6)
Tetrachloroethylene	86 (0.6)
Carbon tetrachloride	86 (1)
1,1,2-Trichloroethane	76 (8)
1,2-Dichloropropane	76 (2)
Trichlorofluoromethane	79 (7)
Trichloroethylene	76 (2)
1,1,1-Trichloroethane	68 (10)
1,2-Dichloroethane	70 (4)
1,3-Dichloropropene	60 (4)
Chlorobenzene	48 (7)
1,2-Dichlorobenzene	65 (5)
1,3-Dichlorobenzene	51 (7)
1,4-Dichlorobenzene	61 (7)
Bromodichloromethane	47 (9)
Bromoform	64 (8)

*Relative standard deviation (percent) in parentheses

detection are the same as for the minicolumn method, and the results obtained by this method are essentially the same as those that would be obtained by the minicolumn method.

A method has been evaluated in the authors' laboratory that employs the carbon adsorption concept but substitutes reductive pyrolysis for oxidative pyrolysis, and conductivity detection for microcoulometric detection of the halide. The reductive pyrolysis–conductivity detection combination was not found to be satisfactory. Problems encountered included poor precision and accuracy, insufficient inorganic chloride rejection, and high variability of system blanks.

Other techniques for measuring organic halide

Another method for measuring OX is the minicolumn method with resin* as the adsorbent.[9] It involves solvent desorption of OX from the resin, controlled combustion of a portion of the solvent sample, and detection by microcoulometry. This method is not preferred because of the unfavorable adsorption–desorption characteristics of some compounds with the resin.

Extractable organic chlorine (EOCl) has been suggested as a useful indicator for chemical pollution in surface water.[10] Extractable organic chlorine has been determined by extraction of the water with petroleum ether, solvent injection and combustion, and measurement by microcoulometry of the total organohalides in the extract. This solvent extraction method is limited to the lipophilic fraction of OX and by variable extraction efficiencies. These limitations are similar to those of the resin procedure previously described. In another study, the determination of extractable organic halogen (EOX) was reported to recover approximately 75 percent of halogenated priority pollutants.[11] Extractable organic halogen cannot, however, isolate these compounds from other lipophilic halogenated organics that may be in the sample and, therefore, when used as a surrogate for priority pollutants, could provide misleading results.

Flash vacuum evaporation, an OX method under study,[12] involves first a desalting step by steam generation and recondensation, followed by the catalytic conversion of organohalides to chlorine (Cl_2). The Cl_2 is then measured by a fluorometric derivatization analysis using syringaldazine.

Neutron activation followed by gamma ray spectroscopy has been used for the analysis of organohalogens. This technique, reportedly first used in Sweden,[13] is receiving increasing attention and is an excellent research tool. The OX can be isolated by solvent extraction or by carbon adsorption. In either case, neutron activation can differentiate between the halogens that comprise TOX. This technique does not, however, fill the need for

*XAD, Rohm and Haas Company, Philadelphia, Pa.

a routine analytical tool that can be used in water laboratories throughout the United States.

The ion chromatograph offers another possibility for detecting and measuring individual halides such as those that would be recovered in a pyrohydrolyzate and reported as OX.[5] Interferences from the sulfur associated with the carbon that is pyrolyzed must be overcome.

Ultrafiltration membranes can be used to separate organic compounds in aqueous solutions on the basis of molecular weight. These separations are not absolute, because some organic matter may be retained as a result of electrical charges on the organics. McCahill, Conroy, and Maier[14] have used this concept to separate OX according to molecular weight. Following separation, the solutions were irradiated with UV radiation to cleave the C-X bond. Chloride alone was determined by ion-specific electrode, whereas Cl^- and Br^- occurring simultaneously were differentiated by ion chromatography. Photolysis required 1.5 h, followed by a typical ion chromatographic analysis time of 0.3–0.5 h. Although no detection limits were given, the ion chromatograph can detect 10^{-7}–10^{-6} *M* halogen with a 1-mL injection.

Purgeable and nonpurgeable organic halides

Direct analysis for purgeable organic halides (POX) is conducted by purging up to a 10-mL aliquot of the water sample into the pyrolysis furnace and titrating the OX in the effluent gas during the purge. Commercially available instruments have a built-in capability for doing this.

Purgeable organic halide can also be estimated by converting data on trihalomethanes (THMs) or other volatile organics to units of Cl^-.[15] Investigations performed in the DWRD laboratory have shown that the loss of some THMs that normally occurs during TOX analysis can be avoided and that the most accurate TOX results are achieved with disinfected water when an estimation of POX from THM analysis is combined with a separate analysis for nonpurgeable organic halide (NPOX).[16] Separate aliquots of the sample must be taken for each analysis. The aliquot taken for NPOX analysis must first be purged free of THMs and can then be analyzed by the carbon adsorption method used for TOX. Purging conditions need not be identical to those of the THM analysis because the THM method compensates for recovery inefficiencies.

When a direct POX analysis is performed in order to combine the results with those of a direct NPOX analysis on an aliquot of the same sample, purging to obtain the POX result and purging the aliquot free of POX prior to NPOX analysis must be of equivalent efficiency. When this condition is met, the combined results give a TOX measurement that agrees with the direct TOX measurement obtained by carbon adsorption.

Generally, whenever either POX or NPOX is determined analytically, the other can be determined by subtraction from the TOX measurement. However, the failure of the TOX measurement to account completely for THMs means that NPOX determined by subtracting POX estimated from gas-chromatographic THM results is low by 10–20 percent.[16]

Measuring disinfection by-products

Disinfectants react with organic materials in drinking water sources to form by-products of largely unknown composition. These reactions have long been recognized in the form of disinfectant "demand" and natural organic color bleaching by chlorine, chlorine dioxide, and ozone. Most of the demand is oxidative; i.e., susceptible sites on the organic molecules are oxidized to new functionalities. In the process, the disinfectant is chemically reduced. On the order of 90 percent of chlorine demand, for example, can ultimately be accounted for as chloride ion. The remaining 10 percent or so may react by substitution or addition reactions and become incorporated into the organic molecular structure. Where Br^- is present, oxidation to active bromine species also occurs, and bromine will be found in the organic by-product.[17]

Some specific compounds that result from this type of reaction have been identified: THMs (which are now regulated), dihaloacetonitriles, trichloroacetic acid, dichloroacetic acid, and 1,1,1-trichloroacetone. These compounds can be identified and measured by gas chromatographic (GC) techniques; however, the compounds detected by these techniques do not account for all of the organic halogen by-products. Some of the other materials are high-molecular-weight, nonvolatile species that are not amenable to GC or other available analytical techniques capable of detecting and measuring specific compounds. Thus, TOX, especially the NPOX parameter, becomes a useful nonspecific measure of the degree of attachment of halogen (Cl, Br, I) in organic molecules that are a result of the disinfection process and, therefore, a useful tool in unit process design and control.

Based on recent findings that organic halogen formation is best avoided in drinking water treatment,[18,19] the nonspecific TOX, NPOX, or POX techniques can be used to measure treatment improvement or deterioration (Figures 1 and 2). The data used to develop Figures 1 and 2 were generated during studies in the DWRD laboratory.[20]

Figure 1 displays the results of free chlorination of a solution of 5 mg humic acid/L.* The study combined three temperatures with three pH values over three reaction periods and involved two chlorine concentrations for each combination. Purgeable organic halide, determined by a THM measurement (essentially all chloroform), is displayed below the abscissa, and NPOX is displayed above. Total organic halide is represented by the total bar. Bromide was not involved in this experimental matrix; the units are given in micrograms as chloride per litre.

In general, THMs are shown in Figure 1 to have increased with reaction pH, whereas NPOX decreased dramatically. At low pH, a temperature increase caused an increase in NPOX that did not occur at neutral and high pH values. Trihalomethane yield increased at all pH values with increasing temperature. Concentrations of NPOX approached their final values faster at high pH than at low pH. This effect was not observed for THMs. Chlorine dosage had a greater effect on NPOX concentrations than on THM concentrations. All of these results of chlorination are typical of those reported for humic materials obtained from other sources.[21]

Figure 2 compares NPOX and THM formation at 20°C at three different pH levels for each of the three disinfectants: chlorine, chloramines, and chlorine dioxide. Formation of NPOX was reduced by 85 percent when chloramines were used instead of chlorine and was much lower still when chlorine dioxide was used. Trihalomethane formation was reduced by 95 percent when chloramines were used, and no THMs were detected when chlorine dioxide was used. Unlike chlorine, which increases the formation of THMs with increasing pH, chloramines and chlorine dioxide resulted in a decrease in the formation of all OX with increasing pH. With chlorine dioxide, formation of NPOX was rapid, with no difference in concentration observed between the 2-h and 144-h samples.

Figures 1 and 2 illustrate the variation in organohalide species formed under different conditions, giving clues of how to minimize OX formation during water treatment. However, this group parameter measures only one specific attribute of the sample's organic matrix, i.e., halogen content. The beginning assumption was that TOX is the most important by-product of concern. It is not, however, a total measure of disinfectant by-product and may not even be proportional to it. This is clear from the data presented in Figure 2, where the oxidant demands were similar for chlorine and chlorine dioxide. Oxidant demand may indeed be a better nonspecific parameter for disinfection by-products if nonhalogenated

*Aldrich Chemical Co. Inc., Milwaukee, Wis.

by-product species are important. Thus, the usefulness of the TOX parameter as a measure of disinfection by-product is limited by a lack of full knowledge of its significance.

TOX as a surrogate for specific chemicals

Total organic halide has been incorporated into federal regulations for monitoring groundwaters near hazardous waste sites.[22] Its use as a surrogate has also been suggested for monitoring individual halogen-containing volatile organic chemicals (halo-VOCs) in waters intended for drinking.[23]

For proper interpretation of TOX or POX results, it is necessary to understand the ability of these analytical techniques to reflect the concentration of specific halogen-containing chemicals, i.e., the appropriate mass balances. Few investigations have been published that correlate TOX and POX analyses with individual VOCs. Early data gave the accuracy of TOX analyses for volatile organohalides as ranging from 73–110 percent (Table 1).[7,24] These halo-VOCs included such compounds as chloroform, bromoform, and bromobenzene in reagent water at concentrations ranging from 98 to 443 μg/L. Data on POX, produced by the same authors,[16,25] indicated 100 percent recovery for chloroform, 98 percent recovery for 100 μg bromoform/L, and 80 percent recovery for 140 μg THM/L. The 80 percent recovery for THMs was obtained with a vitrified insert tube in the pyrolysis system. This was demonstrated to have been the cause of the reduced rates of recovery. Nearly complete recovery of chloroform was obtained when the tube was replaced.

Additional POX recovery data were obtained for a wider variety of halo-VOCs at higher concentrations by Riggin et al (Table 2).[26] These recoveries were also from reagent waters, which had been spiked with 1000 μg compound/L. The researchers reported compound recoveries ranging from 47 to 106 percent, which were from 11 percent (chloroform) to 51 percent lower (bromodichloromethane) than the recoveries previously reported.[7,24]

At lower concentrations of the spiked halo-VOCs, variable recoveries were observed by Riggin et al (Table 3).[26] For 12.5 μg chloroform/L, a complete recovery was obtained. Four other compounds afforded lower recoveries, with bromoform not being detected at 30 μg/L.

More recent data for halo-VOC recoveries were obtained using groundwater that was free of halo-VOCs (Table 4).[27] This groundwater was spiked, headspace-free, with the volatile organics of interest. Each of the compounds was studied at three concentrations: 10, 30, and 100 μ/L. The samples were analyzed in triplicate for both TOX and POX. Purge-and-trap–gas chromatography-electrolytic conductivity detector (P&T-GC-ElCD) analyses were also performed to ensure the integrity of the spiked samples by revealing the presence, if any, of other halo-VOCs. At 10 μg compound/L, which is near to the quantitation limit of the procedures, the recovery range was 79–140 percent for TOX and 25–88 percent for POX. The recoveries of the chlorinated compounds at 30 and 100 μg/L in Table 4 ranged from 55 to 80 percent. There does not appear to be a clear relationship between concentration and recovery, and there may be a more efficient rate of recovery for TOX and POX at the concentrations tested.

Results of a study that involved two laboratories were similar to those just described, with TOX recoveries ranging from 73 to 91 percent and POX recoveries from 56 to 77 percent for bromoform, chloroform, and *t*-dichloroethylene.[28] These data also demonstrate a slight recovery bias in favor of TOX. The results obtained by the two laboratories generally agreed within 10 percent of each other.

The halo-VOC data described have predominantly been from spiked reagent water or a single source of groundwater. The ability of TOX and POX methods to measure halo-VOCs in a variety of groundwaters and the ruggedness of the methods have not been fully investigated. Table 5 gives information on the groundwater sources of several US cities.[27] The TOX in these raw waters ranged from <5–300 μg as Cl^-/L and POX from <2–300 μg as Cl^-/L. The TOX and POX concentrations were compared with P&T-GC-ElCD. Concentrations were reported as Cl^- for individual halo-VOCs. Whereas POX gave a positive result only when halo-VOCs were present in the water, TOX analysis afforded positive results in all but one of the eleven samples. Analysis of five of these positive TOX samples by P&T-GC revealed no detectable halo-VOCs.

Information collected by a USEPA survey also indicated that a background concentration not attributable to halo-VOCs could interfere with the use of TOX as a surrogate for low concentrations of halo-VOCs.[29] An average TOX of 19 μg as Cl^-/L was found in raw groundwater, with a range of from <5 to 85 μg as Cl^-/L. A high TOX (85 μg as Cl^-/L) did not indicate a high halo-VOC concentration, as less than 1 percent could be attributed to halo-VOC in this sample. Surface waters also seem to possess a variable TOX background, ranging from <5 to 49 μg as Cl^-/L. For both groundwaters and surface waters, TOX analysis would have to detect halo-

TABLE 3

*Recovery of low concentrations of selected compounds by POX analysis**

Compound	Spike Level		Recovery of Purgeable Organic Halide	
	μg/L	μg as Cl^-/L	μg as Cl^-/L†	percent
Chloroform	12.5	11	11 (1.4)	100
Trichloroethene	14	10	6 (0.7)	60
Tetrachloroethene	14	10	5 (1.0)	50
Chlorobenzene	25	8	3 (0.6)	38
Bromoform‡	30	13	§	<10

*Average of seven POX analyses[26]
†Standard deviation in parentheses
‡Recovery for bromoform at 300 μg/L (130 μg as Cl^-/L) was 48 percent and 49 percent for duplicate analyses.
§Not detected

TABLE 4

Average accuracy of TOX, POX, and purge-and-trap analyses for groundwater samples spiked with volatile organohalides[27]*

Compound	Concentration μg/L	TOX Recovery percent	POX Recovery percent	Purge and Trap percent of dosed quantity
Bromoform	10.0	140†	62†	120
	30.5	93	66	100
	100	120†	91†	110
Chloroform	10.0	79†	25†	94
	29.9	76	43†	110
	100	81	76	96
t-Dichloroethylene	10.1	84†	53	97
	30.1	63	55	90
	98.4	60	59	99
Tetrachloroethylene	9.83	79†	88†	91
	30.2	75	70†	100
	101	78	70	110

*Based on triplicate analyses for TOX and POX and duplicate analyses for purge and trap
†Precision was >10 percent; the ranges of these percentage relative standard deviations were 15–61 percent at 10 μg/L, 22–25 percent at 30 μg/L, and 27 percent at 100 μg/L.

TABLE 5

Comparison of TOX, POX, and purge-and-trap methods for measuring volatile organohalides in selected groundwaters[27]

City Code	TOX μg as Cl^-/L	POX μg as Cl^-/L	Purge and Trap μg as Cl^-/L
66951	21 (21)	<2	†
66989	10 (56)	<2	0.3 (4)
66952	18 (46)	<2	0.6‡
66990	27 (10)	21 (5)	20 (7)
66954	30 (15)	<2	†
66991	20 (12)	<2	†
66993	25 (27)	<2	†
66998	9 (50)	<2	†
66999	10 (5)	2 (50)	6 (6)
67000	<5	<2	†
Riv[b]	300 (2)	300 (2)	33‡

*Based on triplicate analyses for TOX and POX and duplicate analyses for purge and trap; the percentage relative standard deviation (or percentage difference for purge and trap) is given in parentheses.
†Not detected
‡Single analysis only

TABLE 6

Comparison of costs of analyses

Analytical Technique	Average Cost $	Cost Range $	Number of Laboratories
TOX	99	30–200	33
POX	77	15–140	18
THM (P&T/GC/ElCD)*	86	42–200	15
THM (LLE/GC/ElCD)†	59	40–85	8
Halo-VOC (P&T/GC/ElCD)‡	114	65–150	5
Halo-VOC (P&T/GC/MS)§	207	100–350	18

*Trihalomethane analysis by EPA purge-and-trap methods using an electrolytic conductivity detector
†Trihalomethane analysis by EPA liquid-liquid extraction methods using an electron capture detector
‡Volatile organohalide analysis by EPA purge-and-trap methods using an electrolytic conductivity detector
§Volatile organohalide analysis by EPA purge-and-trap methods using a mass spectrometer detector

VOC concentrations above the background, whose exact nature and variability are yet undefined.

Sample stability

Recent information has shown that certain constituents of TOX are not stable when a water sample is stored after chlorination. This information was first presented at a 1981 meeting of the American Chemical Society in a paper that dealt with the storage of chlorinated drinking waters.[30] The first study, which used samples stored at 20°C from a surface water source, showed a 30 percent decrease in TOX concentration 15 days after addition of sulfite to reduce the chlorine residual (Figure 3). When the chlorine residual was not reduced, a 50 percent increase in TOX was observed. Storage at subambient temperatures (5°C) of sulfite-reduced drinking water from the same source demonstrated a slow rate of decline and a smaller loss (only 10 percent) of TOX. Analysis of THMs, the main component (>90 percent) of the POX, revealed no significant change in concentration. This indicated that the decline resulted from the loss of NPOX and could not be accounted for by hydrolysis to THMs, a reaction that has been observed by others.[21,31-33] These losses may be due to decomposition of the metastable organohalides formed during the chlorination process.[34] A similar 20 percent loss of TOX has been observed in chlorinated groundwater and tertiary effluents after reduction of the chlorine residual.[35] Because of the dominance of continued TOX formation, the losses are not observed in samples not reduced with sulfite.

The storage of sulfite-reduced samples at subambient temperatures is not a guarantee of low NPOX losses. Data for other surface-supplied drinking waters stored under identical subambient conditions show significant loss over time, ranging from a 28 percent loss after 30 days to a peak of 40 percent after 165 days that appeared to be unchanged after an additional 90 days.[34]

Acidifying and refrigerating the sample may solve this problem. When a set of samples was acidified with nitric acid to pH 2, the TOX declined by only 15 percent after three months at room temperature.[34] A second set of samples, whose pH was allowed to remain at 7.9, showed a 51 percent loss during the same period. When acidification was combined with refrigeration (5°C), better preservation was afforded: the acidified samples had no loss of TOX by day 4 and only a 6 percent loss by day 48; the unacidified samples (pH 7.9) suffered a 17 percent decline by day 4 and a 32 percent loss by day 48.

A similar technique uses sulfuric acid and sodium sulfite together with refrigeration to stabilize TOX.[36] The advantage of this technique is that sample bottles containing sulfite and sulfuric acid can be transported to the sampling site by air freight. Nitric acid cannot readily be shipped by air. The effectiveness of sulfuric acid appears to be comparable with that of nitric acid, with only a 9 percent loss of TOX from the sulfite-reduced finished water (surface water source) observed after 39 days of refrigeration.

Availability and cost

Because of the requirements of the Resource Conservation and Recovery Act[37] and general interest in TOX as a surrogate, the measurement of TOX has become widespread. It is estimated there are currently between 50 and 75 commercial laboratories and universities that perform TOX analysis using the instrumentation developed under contract to USEPA.[38]

A survey was conducted by the Technical Support Division of USEPA to determine the capabilities of these laboratories. Of the 33 laboratories contacted, only 18 reported that POX analyses were performed routinely. It is therefore estimated that approximately half of all laboratories performing TOX analyses analyze for POX.

These same laboratories were asked to provide price quotes for measuring TOX, POX, and THMs by purge-and-trap (P&T) and liquid-liquid extraction (LLE) techniques. Also requested were quotes for analysis by P&T of halo-VOCs and identification of the type of detector being used, namely, electrolytic conductivity (ElCD) or mass spectrometer (MS). The cost information is shown in Table 6. Measuring TOX by USEPA Method 450.1 requires duplicate analyses for each sample. This was also applied to POX. The prices for THM and halo-VOC analyses are based on a single measurement, because a duplicate is not required. No information was obtained on the quality of the analytical data generated by these laboratories.

The average costs for TOX and POX analyses were $99 and $77, respectively, with the ranges of cost varying by approximately an order of magnitude (Table 6). Considering the simplicity of measuring POX relative to measuring TOX, it is surprising that average costs and cost ranges are so similar. The fact that TOX measurements are much more routine than those for POX may account for the apparent high cost of POX analysis.

For THM measurements by purge and trap, the laboratories quoted an average price of $86 per sample. For THM measurements by liquid-liquid extraction, the average price quote was $59 per

TABLE 7

Relationship of water sample type, class of organohalide, and response to analytical method

Analytical Method	Method Response*					
	Disinfection By-Products in Finished Drinking Water†			Industrial Synthetic Organics in Source Water and Wastewater†		
	Volatiles (e.g., THMs)	Semivolatiles (e.g., haloacetic acids)	Nonvolatiles (e.g., halohumics)	Volatiles (e.g., TCE)	Semivolatiles (e.g., PCBs)	Nonvolatiles (e.g., dalapon)
TOX	NSNE	NSNE	NSNE	NSNE	NSNE	NSNE
POX	NSNE	NA	NA	NSNE	NA	NA
NPOX	NA	NSNE	NSNE	NA	NSNE	NSNE
P&T-GC	SE	NA	NA	SE	NA	NA
LLE-GC	SE	SE	NA	SE	SE	NA
HPLC	NA	SE	Undefined	NA	SE	SE
D-GC	NA	SE	NA	NA	SE	SE

*NSNE—nonspecific and nonexclusive, NA—not applicable, SE—specific and exclusive

†Water samples have the potential for containing both disinfection by-products and industrial synthetic organics.

sample. The ranges of cost varied approximately fivefold for purge and trap and twofold for liquid–liquid extraction. The data in Table 6 also show that no savings resulted from using TOX analysis (average price $99 per sample) or POX analysis (average price $77 per sample) as a surrogate for THM measurements.

For halo-VOC analysis an average price of $114 per sample was quoted, and a range of $65–$150 was given. This is more expensive than either TOX or POX analysis.

General caveats must be placed on the preceding cost comparisons. The basis for contacting laboratories was their ability to perform TOX measurements using the instrumentation developed under contract to USEPA. Cost data from these laboratories for THM and halo-VOC analyses may not accurately reflect the analytical charges of a wide range of laboratories. The costs, however, appear reasonable to the authors, based on experience in dealing with laboratories specializing in THM and halo-VOC measurements.

Also, although these cost data were valid at the time of the survey (early 1984), little is known about future costs. Sudden increases or decreases in demand for a particular measurement could radically alter costs. Furthermore, consideration is being given to lifting the requirement for duplicate analyses; this could considerably reduce the cost of sample analysis by USEPA Method 450.1.

Selecting an analytical approach

When matching methods to objectives, the first consideration is to establish the needs of the project, whether the project be research, surveillance, or compliance monitoring. In some applications, selecting a methodology capable of providing data of fine distinction and the highest possible precision and accuracy and with stringent quality assurance requirements would be the primary consideration. In more routine applications, perhaps because of high sample volume, cost may be the primary consideration, and a method capable of providing data with a satisfactory but somewhat lesser degree of reliability and less stringent quality assurance requirements may be chosen. Should any uncertainty arise in the course of this latter approach, a more definitive method could be called into use to resolve the question.

Another primary consideration may be the amount of information that the method can provide, e.g., specific compound identification and quantification versus the collective measurement of groups of compounds (a consideration that may be determined by the use of the data).

Table 7 shows the relationship of water sample type to classes and subclasses of target organohalides. In addition, it links the target to the selection of an appropriate method based on the response characteristic of that method.

Response characteristics are generally of three types. The first type is a combination of nonspecific and nonexclusive, meaning that it does not measure specific compounds and cannot measure individual subclasses of compounds to the exclusion of other subclasses to which the method responds. For example, POX analysis will collectively measure THMs and halo-VOCs such as TCE, whether or not measurements for both subclasses are desired.

The second type of response characteristic is a combination of specific and exclusive, meaning that it measures individual compounds to the exclusion of compounds of other subclasses to which the method responds. For example, P&T-GC can measure individual THMs to the exclusion of halo-VOCs such as TCE, simply because of the gas chromatographic character of the method. However, each method of the second type is specific and exclusive only to a degree. This is determined by the details of the test procedures employed.

Exclusivity is of special importance when using the OX methods as surrogates to estimate the presence of a defined subclass of organohalides. For example, in groundwater compliance monitoring, unless there is good reason to believe—perhaps by having previously characterized the water by specific compound analysis—that only the subclass of organohalides of interest is present, an OX measurement may be positively biased by the presence of organohalides other than those of the subclass of interest.

The third type of response characteristic is that a method is not applicable, meaning that the method does not measure a particular subclass of compounds or any individual compounds within the subclass.

The target organohalides defined in Table 7 are differentiated on the basis of their chemical nature and origin. A class separation has been made between chemicals generated by disinfection and those that are generally regarded as industrial in origin. In each category there are volatile, semivolatile, and nonvolatile halogen-containing components. Of course, certain chemicals may be of volatility intermediate to these subclasses. Table 8 lists those methods considered by the authors to provide the most reliable measure of the various subclasses of organohalides for the activities discussed.

Disinfection by-products. For disinfection by-products, the volatile compounds are comprised principally of THMs. Semivolatile chemicals such as the dihaloacetonitriles and chloroacetones occur at much lower concentrations than THMs. Although the conditions were far more severe with regard to precursor and oxidant concentration than those normally encountered in treatment practice, it has recently been reported that a substantial portion of the semivolatile fraction is composed of lower-molecular-weight haloacetic acids.[39] The nonvolatile fraction includes halogenated precursor material, much of which is of high molecular weight.

For the analysis of volatile disinfection by-products, purge-and-trap or liquid–liquid extraction gas chromatography is preferred over a TOX, NPOX, or POX measurement because GC analysis pro-

TABLE 8

Most reliable analytical methods for various subclasses of target organohalides

Analytical Method	Disinfection By-Products			Industrial Synthetic Organics		
	Volatiles (e.g., THMs)	Semivolatiles (e.g., haloacetic acids)	Nonvolatiles (e.g., halohumics)	Volatiles (e.g., TCE)	Semivolatiles (e.g., PCBs)	Nonvolatiles (e.g., dalapon)
TOX	S*	S*	S*	S*	S*	S*
POX			S*	S*		
NPOX	X					
P&T-GC			X	X		
LLE-BG		X	X	X	X	
HPLC					X	X
D-GC		X				X

*Currently useful as a screening procedure

vides significantly more information, namely, the identities and concentrations of specific compounds. The time and cost of analysis are approximately the same for organohalide and GC procedures because USEPA Method 450.1, unlike the other methods, requires duplicate analyses on every sample.

Duplicate analyses of every sample were originally required in the context of drinking water research activities that needed greater stringency of quality control because of small differences and difficult-to-measure OX concentrations. The requirement may eventually be lifted for surveillance and monitoring activities that do not need fine distinctions between measurements. When fine distinctions are needed, this requirement may be applied to all analytical methods.

For many nonvolatile by-products, no alternative to organohalide measurement (NPOX) exists, because either analysis for specific organics cannot be performed or the compounds are unknown, difficult to measure, or both. Certain semivolatiles such as the chloroacetic acids, however, are amendable to LLE and derivitization-gas chromatography (D/GC), which is included in Table 7. Techniques such as column chromatography and high performance liquid chromatography (HPLC) are being used to identify higher-molecular-weight by-product fractions, generally in research investigations.

The only way to directly measure nonvolatile by-products (NPOX) is by using the method for TOX on a sample that has been completely purged of volatiles. If POX is then measured on a duplicate sample using a method of purging that is of equivalent efficiency, the sum of the POX and NPOX is equivalent to the TOX.[16] Alternatively, an indirect measure of NPOX can be obtained by measuring directly and subtracting the POX concentration from the TOX concentration.[16]

Both TOX and NPOX are measured to an unknown degree of accuracy because there exists no reference material for humic and fulvic acids with which to assess recovery efficiency by carbon adsorption. The only estimate of accuracy comes from comparing total organic carbon (TOC) measurements before and after a sample has been put through the carbon. The efficiency of removal of TOC has been determined to be 90-95 percent[23] and is assumed to be the same for TOX.

Industrial contaminants. Measurements of POX and TOX have been evaluated as surrogate measures of halo-VOCs that are industrial in origin. In most cases, analyses for specific compounds are suggested, because more information can be obtained than by measuring surrogates, if costs and time are comparable. However, the potential does exist for using the POX measurement as a surrogate measure of halo-VOCs. The cost survey reported in Table 6 indicated average costs of $77 and $114 for POX and P&T-GC analyses, respectively. In certain situations, analysis for POX may become the preferred tool with which to screen for halo-VOCs, provided that it is firmly established that duplicate analyses on every sample are not required and that sufficient data have been acquired on a variety of surface and groundwaters to adequately demonstrate the relationship between POX and halo-VOC measurements.

Semivolatile and nonvolatile industrial synthetic organohalides may be analyzed by the TOX and NPOX methods, LLE-GC, and other chromatographic techniques such as HPLC and D/GC. The relationship between these surrogate and nonsurrogate parameters has not been adequately shown. Some waters contain OX materials that are not accounted for by chromatographic techniques, and the accuracy of OX by carbon adsorption is uncertain.

Specific chemicals should be measured if this can be accomplished at reasonable cost. However, the wide variety of organohalides that may exist at a given site, such as landfills, can make TOX or NPOX measurements cost effective as a screening tool for halogen-containing organics. If a high TOX or NPOX value were obtained during screening, measurements of specific compounds would then be attempted.

Summary and conclusions

Measurements of surrogates and of specific compounds can be useful in assessing water quality. In some cases, analyses for specific chemicals provide the required information. In other situations, however, individual halogen-containing chemicals cannot be measured easily or at all, and POX or NPOX measurements are a useful indicator of chemical content. For a survey of possible organohalide contamination, OX measurements may be satisfactory as a prelude to more detailed analysis or simply as an early-warning indicator.

An important application of OX measurements is in unit process design, control, and monitoring. Measurement of OX in wastewater primarily discerns compounds of industrial origin, whereas analysis of OX in finished drinking water primarily discerns disinfection by-products. Trihalomethane and NPOX data generated under carefully controlled "treatment" conditions can lead to a plant design that minimizes the formation, and thus the concentration, of halogenated disinfection by-products in the treated water. Halogenated by-products can be monitored and, to some extent, controlled in plant operation.

From a health standpoint, minimizing these halogen-containing chemicals is assumed to be desirable, but in most cases an attempt is being made to control chemicals that cannot be directly measured. Placing a value on this type of measurement is difficult because of the uncertainty about whether specific chemicals of health concern have in fact been controlled. In addition, chemicals that do not contain halogens are not being considered. Controlling OX disinfection by-products may have little or no relationship to the control of compounds that do not contain halogens but are of health concern.

Many water samples have the potential for containing both disinfection by-prod-

ucts and industrial synthetic organics. Organohalide methods, being nonexclusive, have the hidden potential for biasing any attempted exclusive measure of either class of target organohalides.

In spite of its shortcomings, the TOX method has a unique advantage in that it can verify the absence of OX contamination without the need to resort to a variety of specific methods to eliminate all the possibilities. Costs can be saved by using a single method to monitor a situation in which two or more methods might otherwise be required. To demonstrate the absence of either volatile organohalides or nonvolatile organohalides, measuring POX and NPOX can be used to similar advantage.

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